

## Addition of a phosphine ligand switches an N-heterocyclic carbene-zirconium catalyst from oligomerization to polymerization of 1-hexene†

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**A catalyst for the oligomerization of 1-hexene, generated by the activation of a benzimidazolydene zirconium dibenzyl complex, switches to a polymerization catalyst on addition of a trialkylphosphine.**

Polyolefin production is practiced on an extremely large scale.<sup>1</sup> Over the past 20 years there have been significant advances in the development of homogeneous single-site catalysts. Well-defined early transition metal metallocene catalysts have facilitated studies on the fundamental mechanistic features of polyolefin catalysis.<sup>2</sup> More recently, “post-metallocene” complexes bearing multidentate oxygen- and nitrogen-based ligands have proven to be good alternatives as catalysts for ethylene polymerization;<sup>3</sup> however,  $\alpha$ -olefins still present challenges to non-metallocene catalysts, which often show poor to only moderate activity and/or rapid deactivation, thus affording only traces of oligomers or polymers.<sup>4</sup> Furthermore, the factors that determine oligomerization *vs.* polymerization of  $\alpha$ -olefins are unpredictable: subtle changes in the ligand framework, the co-catalyst, and the reaction conditions can all affect the reactivities and selectivities of these catalyst systems. As part of our studies on early transition metal complexes of tridentate NHC ligands in catalysis,<sup>5</sup> especially for olefin oligomerization/polymerization,<sup>6</sup> we report here on a bis(phenolate)benzimidazolydene zirconium based catalyst that can be switched between oligomerization and polymerization of 1-hexene by the simple addition of tertiary phosphines. While this work was in progress, a report appeared of a highly regioselective 1-hexene oligomerization catalyzed by a closely-related NHC-

zirconium complex activated by anilinium; in that case, coordination of the dimethylaniline byproduct was suggested to account for the selective behavior.<sup>6g</sup>

The (OCO) ligand **1** is obtained by cyclization of *N,N'*-bis(3,5-di-*tert*-butyl-phenol)-1,2-phenylenediamide<sup>7</sup> with triethylformate in the presence of hydrochloric acid in 74% yield (Scheme 1). Subsequent reaction of **1** with one equivalent of KHMDS followed by addition of tetrabenzylzirconium affords (OCO)ZrBn<sub>2</sub> (**2**) in 88% yield. The <sup>13</sup>C NMR spectrum reveals a characteristic downfield signal ( $\delta$  199.9 ppm) assigned to the C<sub>carbene</sub>-Zr carbon.

Crystals of **2** suitable for X-ray diffraction were obtained from a cold diethyl ether solution. The unit cell contains two independent molecules exhibiting a distorted trigonal bipyramidal geometry about zirconium (only one is shown in Fig. 1) with very similar structural parameters. The benzimidazolydene moiety is non-planar, lying outside of the O(1)-Zr-O(2) plane.<sup>8</sup> One of the two benzyl groups adopts a pronounced  $\eta^2$  binding mode (Zr(1)-C(36) = 2.30 Å; Zr(1)-C(37) = 2.64 Å; Zr(1)-C(36)-C(37) = 86°; *cf.* Zr(1)-C(43) = 2.27 Å; Zr(1)-C(44) = 2.82 Å; Zr(1)-C(43)-C(44) = 95°), a common feature of electron-deficient five-coordinate dibenzylzirconium complexes.<sup>4c,9</sup>

Activation of complex **2** with one equivalent of [Ph<sub>3</sub>C]-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] generates a catalyst for 1-hexene oligomerization/polymerization at room temperature. With no additive, oligomerization is observed: GC analysis shows a roughly Schultz-Flory distribution between C<sub>12</sub> and C<sub>42</sub> with a maximum at the tetramer (Table 1, entry 1); MALDI-TOF analysis<sup>10</sup> reveals that the distribution extends to at least C<sub>78</sub> ( $n = 13$ ). A second addition of 1-hexene after 14 h was partially consumed (68% conversion), demonstrating some remaining activity of the catalyst.<sup>11</sup>

The nature of the end-group in the resulting oligomers was addressed by <sup>1</sup>H NMR spectroscopy, revealing the presence of vinylene R<sup>1</sup>CH = CHR<sup>2</sup> ( $\delta$  = 5.4 ppm) and vinylidene H<sub>2</sub>C = CR<sup>1</sup>R<sup>2</sup> ( $\delta$  = 4.8 ppm) resonances in an 85 : 15 ratio respectively (Fig. S6†).<sup>11</sup> This result suggests a preference for the formation of the oligo(1-hexene)s by  $\beta$ -H-elimination following 2,1-enchainment of the monomer.

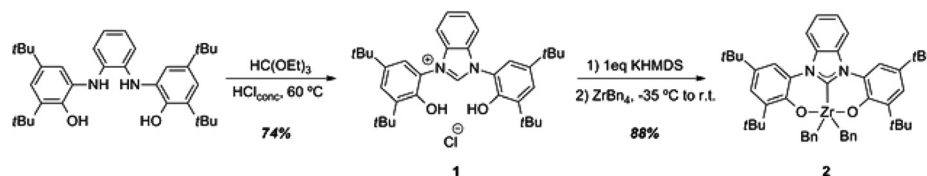
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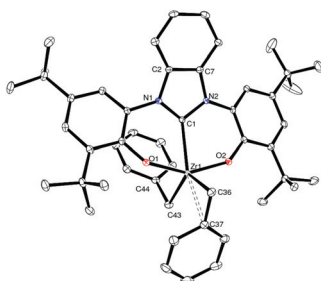
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†Electronic supplementary information (ESI) available: Experimental procedures, crystallographic data and catalytic details (GC traces, MALDI-TOF, NMR of oligomers/polymers). CCDC 942447. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52342j



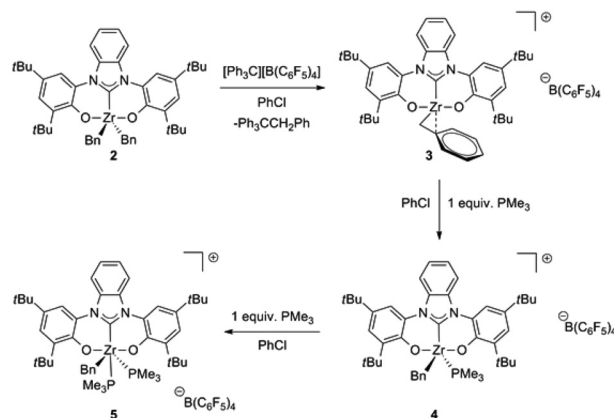
**Scheme 1** Synthesis of the benzimidazolium chloride **1** and its zirconium complex **2**.



**Fig. 1** Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°): Zr(1)–C(1) = 2.3358(17), Zr(1)–O(1) = 1.9957(12), Zr(1)–O(2) = 1.9953(11), Zr(1)–C(36) = 2.3038(17), Zr(1)–C(37) = 2.6406(17), Zr(1)–C(43) = 2.2737(18), Zr(1)–C(44) = 2.8246(16), Zr(1)–C(36)–C(37) = 85.91(10), Zr(1)–C(43)–C(44) = 95.49(11).

When  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  is used instead as the stoichiometric activator, only a very low conversion (~5%) of 1-hexene is observed.<sup>11</sup> This is likely due to the coordination of the dimethylaniline byproduct generated on activation, which blocks the approach of the olefin. Indeed, a similar behavior is observed when sterically hindered 2,6-lutidine is added to the  $2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  system (conv.: <1%). Addition of phosphine ligands results in a more complex behavior. Triphenylphosphine does not perturb the system, giving essentially the same yield and distribution of oligomers as that when no additive is used (Table 1, entry 2), while tricyclohexylphosphine completely inhibits activity. Surprisingly, the addition of one equivalent of triethylphosphine or trimethylphosphine results in the formation of poly(1-hexene) (Table 1, entries 3 and 4); by  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy, both polymers are atactic with average molecular weights of 10 545 and 2965 respectively, and contain a predominance of vinylidene end groups (Fig. S8 and S10†).<sup>11</sup> Addition of two equivalents of triethylphosphine leads to complete inhibition of catalysis.

NMR studies on this system are consistent with the structures proposed in Scheme 2. Addition of complex **2** in



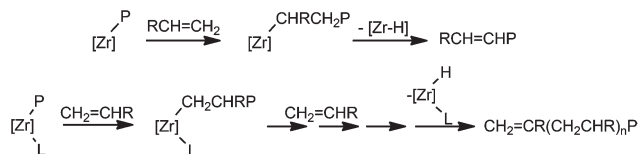
**Scheme 2** Proposed species generated by the activation of **2** with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  followed by addition of  $\text{PMe}_3$ .

chlorobenzene to  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  at  $0\text{ }^\circ\text{C}$ <sup>12</sup> results in the clean and quantitative formation of what appears to be cationic zirconium complex **3**, as indicated by the downfield shift of the benzyl  $\text{CH}_2$  group ( $\delta$  2.94 in  $^1\text{H}$  NMR; 71.3 in  $^{13}\text{C}$  NMR), along with one equivalent of  $\text{Ph}_3\text{CCH}_2\text{Ph}$ . Only a slight difference in the carbene chemical shift is observed between the cationic (**3**) and the neutral (**2**) complexes ( $\delta$  196.0 for **3** vs. 199.9 for **2**). The benzyl ligand appears still to be coordinated in a  $\eta^2$  fashion, as indicated by the large coupling constant ( $J_{\text{CH}} = 142\text{ Hz}$ ).<sup>13</sup> Addition of one equivalent of trimethylphosphine results in the formation of what appears to be cationic phosphine adduct **4**, which displays a singlet resonance ( $\delta$  –20.2) in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The benzyl group resonances shift considerably relative to complex **3** ( $\text{CH}_2$  group  $^{13}\text{C}$ :  $\delta$  63.2 for **4** vs. 71.3 ppm for **3**; phenyl group  $^1\text{H}$ :  $\delta$  [7.7–7.2] for **4** vs. [6.5–6.2] ppm for **3**), suggesting  $\eta^1$  coordination in **4**. Addition of a second equivalent of trimethylphosphine gives the bis(trimethylphosphine) adduct **5**, indicated by the appearance of an AB quartet in the  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\delta$  –28 and –32 ppm with  $J_{\text{PP}} =$

**Table 1** Oligomerization/polymerization of 1-hexene using complex **2**<sup>a</sup>

Entry	Additives	Conv. (%)	C <sub>12</sub> (%)	C <sub>18</sub> (%)	C <sub>24</sub> (%)	C <sub>30</sub> (%)	C <sub>36</sub> (%)	C <sub>42</sub> (%)	Higher oligomers	Polymer (g, Mn <sup>b</sup> )
1	None	89	7	7	15	13	11	5	31	<0.02
2	PPh <sub>3</sub>	96	7	6	16	15	13	6	33	<0.02
3	PEt <sub>3</sub>	99	0	0	0	0	2	6	n.d.	0.48, 2965
4	PMe <sub>3</sub>	99	0	0	0	0	0	0	n.d.	0.49, 10 545

<sup>a</sup> Conditions:  $[\mathbf{2}] = [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] = 0.006\text{ mmol}$ ; 1-hexene (0.53 g, 6.3 mmol); additive (1 equiv., 0.006 mmol), room temperature; reaction time: 14 h. Oligomers were analyzed by GC. <sup>b</sup> Calculated by integration using  $^1\text{H}$  NMR spectroscopy of olefinic end groups relative to aliphatic groups.



**Scheme 3** Proposed explanation for the ligand-induced shift from oligomerization to polymerization. P = growing chain.

99 Hz);<sup>14</sup> the benzyl CH<sub>2</sub> <sup>13</sup>C resonance ( $\delta$  61.2) is close to that for **4**. <sup>19</sup>F NMR spectra for complexes **3**, **4** and **5** are indicative of solvent separated cation/anion pairs.<sup>11</sup> Addition of 1-hexene to complex **5** results in no reaction, even after 5 hours at room temperature.

The oligomerization/polymerization of 1-hexene was followed over time in the absence and presence of trimethylphosphine. When no additive is present, conversion of the 1-hexene is approximately 60% complete after 60 minutes, and reaches its maximum value (~89%) after 5 hours at room temperature.<sup>11</sup> On the other hand, when one equivalent of trimethylphosphine is present, the consumption of 1-hexene is slightly exothermic and rapid (no trace of remaining 1-hexene is observed by GC after 30 minutes).

A model that can account for these ligand effects and is consistent with all observations is shown in Scheme 3. In the absence of added ligand, 2,1-insertion of the monomer into a growing polymer chain is preferred, and termination by  $\beta$ -H elimination of the resulting  $\alpha$ -substituted alkyl is relatively fast compared to further growth, leading to a predominance of oligomers with vinylene end groups. Addition of a ligand such as PMe<sub>3</sub> or PEt<sub>3</sub> increases steric crowding, changing the regio-preference to 1,2-insertion, giving an  $\alpha$ -unsubstituted alkyl that is less prone to  $\beta$ -H elimination relative to growth, and hence a predominance of polymers with vinylidene end groups is obtained. Coordination of a still larger ligand (dimethylaniline, 2,6-lutidine, PCy<sub>3</sub>) increases crowding so much that olefin coordination is completely blocked, as does addition of a second smaller PR<sub>3</sub>; PPh<sub>3</sub> apparently binds more weakly and does not compete with olefin coordination.

The reason for the acceleration of monomer conversion with the addition of PR<sub>3</sub> is less clear, but the complexity of kinetics in such systems, where any of a number of steps involving initiation, propagation or termination may strongly affect the observed rates, leaves many possibilities open. Examples of both acceleration and retardation by additional ligation have been observed previously.<sup>4j,6g</sup> Mechanistic studies are ongoing in our labs in the hope of reaching a more complete and conclusive explanation for the dramatic ligand “toggle” effect reported here, which would be an important step in the much larger project of understanding the subtle connections between the catalyst structure and catalytic behavior.

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